A study of absorption currents in poly(methyl methacrylate) (PMMA) : polyvinyl acetate (PVAc) blend films

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Abstract : The absorption currents measured in discharge mode with poly(methyl methacrylate) (PMMA) : poly(vinyl acetate) (PVAc)-blend films (≈ 20 μm) as a function of poling field [(2.0–5.0) × 10^4 V/cm], temperatures (313–353 K) and polymer weight ratio (90 : 10 and 80 : 20) have been found to follow Curie-von Schweidler law, characterized with two slopes in short and long time regions. The curves become steeper at longer times. Isochronals characteristics constructed from these data seemed to reveal a broad peak observed at 353 K The activation energy values are found to increase with PVAc content and also with time of observation. The various observed characteristics are considered to be due to space charge origin alongwith contribution from dipolar-groups.

The movement of charge carriers in polymeric dielectrics has received a great attention because of its importance in science and technology [1–3]. However, despite of a large amount of efforts made over the last decade [4–6], there remains substantial doubt as to the mechanism of charge transport in many insulating polymers which find very wide industrial applications. There are various methods of studying conduction processes [7] which include AC conduction studies, charge particle bombardment surface voltage decay, trapped charge decay, radiation induced conduction and photo conduction *etc*. However, there are uncertainties in measurements inherent in each of the above methods. In view of such uncertainties, it is suggestive to have a renewed attack upon an old problem that of time dependent dielectric absorption/desorption currents which flow, following the application or removal of voltage.

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A systematic analysis of the transient currents has indicated how a combination of time, temperature and field dependence can lead to a fairly unambiguous conclusion as to the injection mechanism and the amount of trapping taking place. The origin of absorption and resorption current is still the subject of much controversy and various mechanism have been proposed to explain the transient current [5–10].

A lot of work on charge storage has been carried out on poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) using various techniques [11–16]. The physical processes leading to electret state of these polymers are tolerably clear. However, the effect of blending of these two polymers on charge storage and transport mechanisms is still not well understood. It has been-shown that polymer blends are better charge storer [17,18] than those of the individual components. In view of these considerations, it is interesting to study the transient currents of PMMA and PVAc blends, which may give information about the molecular interaction and the extent of mixing between the two individual components and will enable us to understand the nature of microscopic mechanism responsible for charge storage and transport in the polyblend.

The present note reports the effect of various parameters such as poling field, temperature and time on the transient current in a blend of PMMA and PVAc. ·

Isothermal immersion technique was utilised for preparing films of polyblends. Polyblend films were prepared by dissolving the two polymers, in required proportion. in a common solvent chloroform. The two blend samples prepared were 90 : 10 and 80 : 20, by weight proportion of PMMA and PVAc, designated as P_1 and P_2, respectively. The solution was prepared in a glass beaker by first dissolving 2.1 g PMMA in 30 ml of chloroform at room temperature. Appropriate amount of PVAc was then mixed in it. The solution was continuously stirred for about 30 min by means of a teflon-coated magnetic stirrer. Thereafter, it was stirred and heated upto 313 K to yield a homogeneous solution. The glass beaker containing the solution was then immersed in a constant temperature oil bath. Ultrasonically, cleaned vacuum aluminized microscopic glass slides were immersed vertically into the solution for a period of 30 min. After the deposition of film, the glass slide was taken out and dried in an oven at 313 K for 24 h to remove all the traces of the solvent. This was followed by room temperature outgassing at 133.33×10^{-5} Newton/m^2 for a further period of 24 h. Upper metal electrode was also vacuum deposited [19,20]. The thickness of the samples was of the order of $\approx 20 \ \mu m$, which was estimated [21] by measuring the capacitance of fabricated sandwiches taking the value of dielectric constant ε of PMMA and PVAc as 3.

Figure 1 shows the variation of current in discharge mode for P_1 and P_2 samples polarized with 2.0×10^4 V/cm at polarizing temperatures of 313, 323, 353, 343 and 353 K. There is a difference in the order of discharge current for sample P_2 as compared to the order noticed for sample P_1. Figure 2 depicts such currents for samples P_1 and P_2 polarized at 313 K with various poling fields $(2.0–5.0) \times 10^4$ V/cm. As can be observed from Figure 1, the magnitude of the discharge currents at a particular time show a marked

dependence of temperature *i.e.* an increase in the value of the current for the entire temperature range of 313 to 353 K. The various plots have been found to be characterized
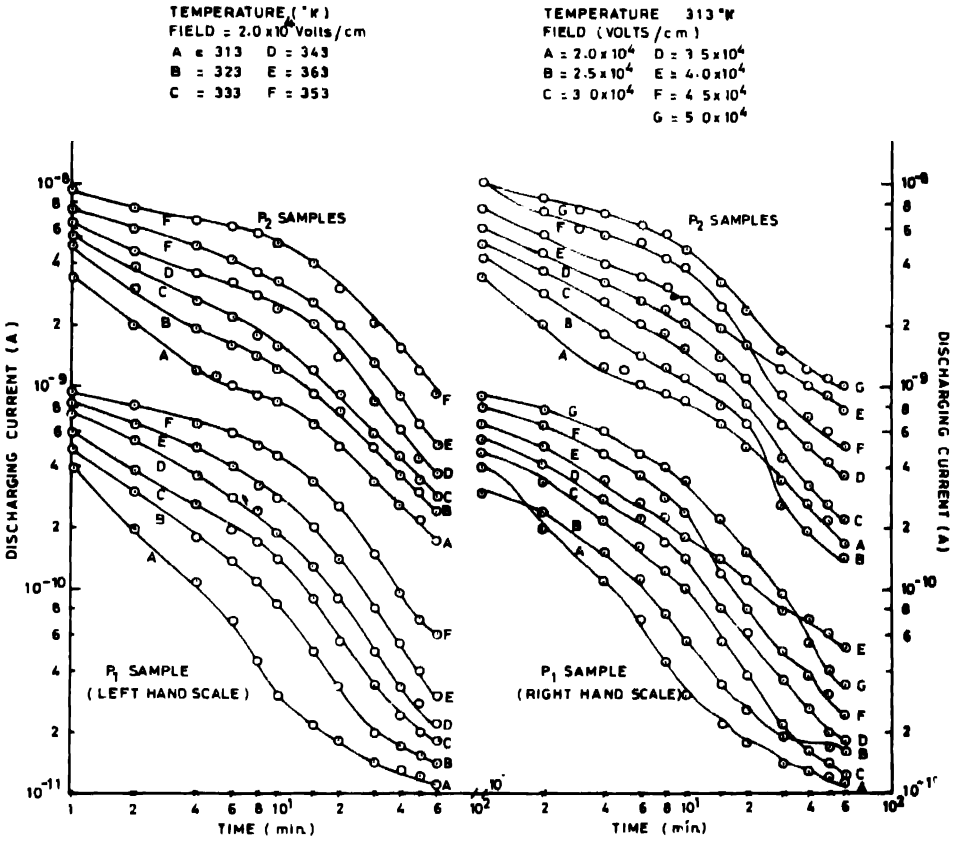

Figure 1. Current transient *versus* time curves at various temperatures (313, 323, 333, 343 and 353 K) with constant poling field (2.0 × 10⁴ volts/cm) for P_1 and P_2 samples.

Figure 2. Current transient *versus* time curves with various poling fields (2.0 × 10⁴, 2.5 × 10⁴, 3.0 × 10⁴, 3.5 × 10⁴, 4.0 × 10⁴, 4.5 × 10⁴ and 5.0 × 10⁴ volts/cm) at 313 K, for P_1 and P_2 samples.

with two regions; one, short time region and the other long time region. The curves become steeper at longer times. The value of slope(n) found for samples P_1 and P_2 become smaller (≈ 0.5) for short time region, as the time of discharge increases, while that for long time region an increase in the value of n almost approaching to 1.73, is obtained. There appears to be a process of thermal activation over the whole range of temperature. The observed time dependence of the current transients may be represented by the Curie-von Schweidler law

$$I_a(t) = A(T) t^{-n} \tag{1}$$

where, I_a is the absorption current, t the time and $A(T)$ a temperature-dependence factor. The faster decay of current in long time region for different samples indicates the existence of

energitically distributed localized traps in the sample. Trapping of charges can take place at various trapping sites-surface states, chain foldings and molecular disorder [22]. It seems that at lower charging temperatures only shallow traps are involved which get emptied at these temperatures. But as the time rises, more and more deeper traps are involved. The trapping of charge carriers (holes and electrons) in the deep trap levels may lead to induced dipole formation [23]. The discharge currents measured for P_1 and P_2 samples at constant times (isochronals) plotted against temperature are shown in Figure 3. These plots are characterized by a well defined peak at 353 K. It should be mentioned here that the thermally stimulated discharge current peak of this sample [24] which is due to induced
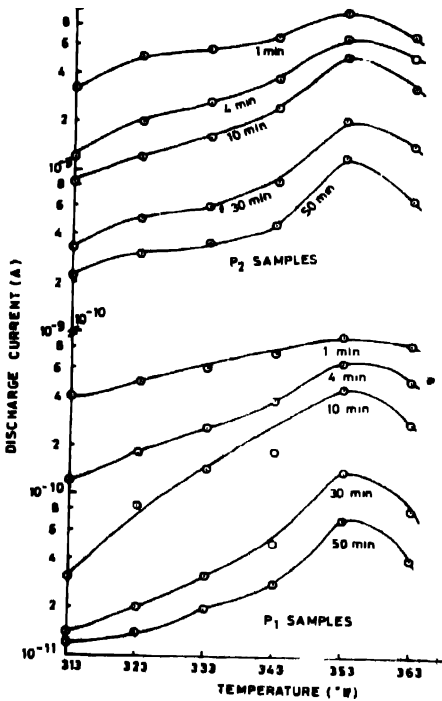

Figure 3. Current transient *versus* temperature curves at constant times (1 min, 4 min, 10 min, 30 min and 50 min) for P_1 and P_2 samples.

dipoles, is at the same temperature as the isochronals peak for different times. The activation energy value obtained from activation plots of the discharge current at various prescribed times for P_1 and P_2 samples are found to vary between 0.78 to 1.38 eV. The large value of activation energy in the present case may be taken as an indication of induced dipole formation because in this case the energy required to disorient them and subsequently release charge carriers from the trapping sites is expected to be higher [17,18]. The value of activation energy agrees well with the value obtained from the TSDC results [24]. For samples with a fixed weight ratio of the two polymers, the activation energy value has been found to increase with increase in time of observation of the discharge current and also with increasing concentration of polymer at fixed time.

It is evident that the magnitude of current increases with increase in the concentration of PVAc in PMMA. This can be understood by assuming that polyblends are mixtures of two homopolymers and the chances of charge trapping in them at the interfaces are much more than in the individual homopolymers. Increasing concentration of PVAc in the polymer blend compound is considered to play an important role in modifying the trap structure in the sample causing more and more deeper traps which leads to the induced dipole formation, due to which the observed activation energy value is more. It seems reasonable to suggest that the C=O group may represent a major fraction of the localized centres by which the transport of the injected electrons takes place. The polyblend samples used in the present case are expected to possess various dipoles due to the presence of PMMA. Poly(vinyl acetate) has a weak permanent dipole moment. Poly(methyl methacrylate) (PMMA) contains the ester side groups $COOCH_3$, which is polar, while PVAc has polar group C=O in the side chain. These polar groups form permanent dipoles which can be oriented during the polarisation process. In the segments, mobility may be increased after the complete phase transition and thus the possibility of injection of charge carriers near the electrodes and their drift seem to be possibly by self motion of charge carriers/ions above the T_g range. Above T_g, a sudden change in its volume may occur and thus structural rearrangements of chains (segments) may be possible due to sufficient mobility of segments. Below T_g, it does not change with temperature. These considerations suggest that it is reasonable to ascribe the observed discharge current due to the dipolar mechanism. However, the experimental facts in the present case are not consistent with the behaviour of discharging current. In the case of dipolar mechanism, the discharging current should vary linearly with the field intensity. However, in the present case, the discharging current depends on fields in at random manner (Figure 2). The various facts including the weak polar nature of polymers, observed values for shorter and longer times and thermal activation of current over certain temperature range as observed in the present case indicate that the space charge due to accumulation of charge carriers near the electrodes and trapping in the bulk may be supposed to account for the observed current. Later these charges form induced dipoles which get oriented inside the sample in the presence of step field. The reorientation of these induced dipoles gives rise to a peak in the isochronals as shown in Figure 3. In the case of transients governed by space charge, the peak in the current time curve should occur at a time

$$t_m = 0.786 \, a^2 \, / \, \mu V$$

where V is the applied voltage, a is the sample thickness and μ the carrier mobility. To have a rough estimate of the time at which this peak should occur we used the values of a, V and μ to be 20 μm, 2.0×10^4 volts/cm and 10^{-11} cm^2/Vs. It was found that t_m should approximately be equal to 1.576×10^3 S. Thus, there is every possibility of space charge relaxation occurring at sufficiently longer times. This may be due to trapping of charge carriers in sufficiently deeper traps. Tunneling current should be independent of temperature and proportional to the field at modest fields. In the present case, currents at various fixed times have been found to be thermally activated in a particular temperature

range. This observation eliminates tunneling as a possible mechanism for the observed transient currents. In the case of electrode polarization the values of n are reported [25] not exceeds 0.5 at short times and $n > 1$ for long time. However, in the present case at shorter times, value of n varies from 0.41 to 0.5, while at longer times it varies from 0.87 to 1.73. Thus, this mechanism seems also not to be operative in the present case. The hopping mechanism is considered to lead to the increase in activation energy which is observed to decrease with increase in time. Such behaviour suggests that hopping of charge carriers is not expected to occur in the present case.

Struik [26] showed that solids like polymers are not in thermodynamic equilibrium at temperatures below their glass transition. For such materials, free volume enthalpy and entropy are greater than those they would be in the equilibrium state. The gradual approach to equilibrium affects many properties for example, free-volume of the polymer may be decreased. The decrease in free volume lowers the mobility of the chain segments and also charge carriers such as ions. The decrease in mobility may be expected to reduce dc conductivity. At higher electric fields, the change in mobility may take place faster than that at lower fields and also recombination of charge carriers may move.

Considering the effects of various parameters on the obsorption current in PMMA : PVAc blend, we conclude that the polarization in the blend is due to trapping of the bulk charges, produced charges as well as the electrode injected charges in the deeper traps and their subsequent alignment due to the step field.

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